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# Catalytic Oxidation of 1,1-Dichloroethane

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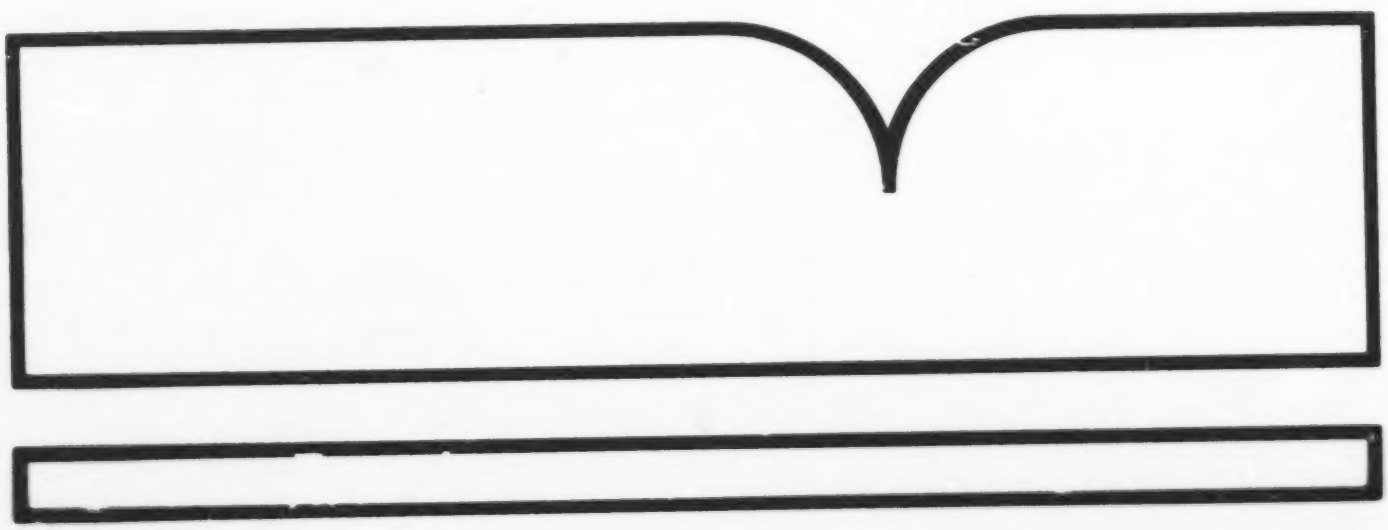

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16. ABSTRACT The paper gives results of an investigation of the catalytic oxidation of 1,1-dichloroethane over a commercial $Cr_2O_3/Al_2O_3$ catalyst at 500 ppm and 30-500 C. Vinyl chloride was observed as an intermediate in the oxidation process, being formed to significant extents between 230 and 330 C. This suggests HCl abstraction as the first step in the catalytic oxidation process. Similar experiments on 1,1,1-trichloroethane showed the presence of a 1,1-dichloroethylene intermediate, supporting the HCl abstraction hypothesis. In both cases, no carbon-chloride bonds were left at 500 C. No significant CO formation was observed, with the material balance on carbon atoms being satisfied by $CO_2$ at 500 C.

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# Catalytic Oxidation of 1,1-Dichloroethane

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**Abstract**—The catalytic oxidation of 1,1-dichloroethane was investigated over a commercial $Cr_2O_3/Al_2O_3$ catalyst at 500 ppm and 30 to 500°C. Vinyl chloride was observed as an intermediate in the oxidation process, being formed to significant extents between 230 and 330°C. This suggests HCl abstraction as the first step in the catalytic oxidation process. Similar experiments on 1,1,1-trichloroethane showed the presence of a 1,1-dichloroethylene intermediate, supporting the HCl abstraction hypothesis. In both cases, no carbon-chlorine bonds were left at 500°C. No significant carbon monoxide formation was observed, with the material balance on carbon atoms being satisfied by carbon dioxide at 500°C.

*Key words*: catalyst, oxidation, 1,1-dichloroethane, dehydrochlorination, vinyl chloride.

## INTRODUCTION

Chlorinated hydrocarbons are widely used in, and emitted from, many industrial processes. These compounds are known to be hazardous to the environment and public health. Catalytic oxidation is one option for the control of these emissions.

Previous research in the heterogeneous catalytic oxidation of low concentrations of chlorinated hydrocarbons in air has focused on identifying highly active catalysts and final reaction products at temperatures high enough for essentially complete oxidation. Little work has been reported on the product distribution at intermediate temperatures and the reaction pathways leading to these products.

Numerous catalysts have been tested for the oxidation of chlorinated hydrocarbons in air. As a general rule, catalysts that have shown the most activity and resistance to deactivation are either single or mixed metal oxides (Musick and Williams, 1974; Laidig *et al.*, 1981; Kageyama, 1974; Sare and Lavanish, 1977 a, b, c; Lavanish and Sare, 1977). Supported platinum (Yang and Reedy, 1977), chlorinated platinum on alumina (Lindberg *et al.*, 1977) and platinum/metal oxide (Bond and Sadeghi, 1975) catalysts have also been examined, however. From this work, an approximate ranking of simple catalysts in terms of activity can be made. Laidig *et al.* (1981) tested several vanadia catalysts, $Pt/Al_2O_3$, and a $Cr_2O_3$–$CuO/Al_2O_3$ for the oxidation of $CHCl_3$. The most active (judged by overall conversion and $CO_2$ formation) and most deactivation-resistant catalyst was $Cr_2O_3$–$CuO/Al_2O_3$. Pope *et al.* (1978) found that a $Co_3O_4$ catalyst was much more active than a Pt/honeycomb catalyst in oxidation of 1,1,1-trichloroethane. Manning (1984) tested a 12.5 wt % $Cr_2O_3/Al_2O_3$ fluid bed catalyst in the oxidation of $CH_2Cl_2$ and three chlorinated ethylenes and showed it to be an active catalyst. The activity of simple, single metal oxides for the complete oxidation of chlorinated compounds may be summarized as follows:

$$Co \sim Cr > Mn > Cu > Ni > Pt > V > Mo$$

This ranking approximates the more general one of Germain (1972) for a wide range of oxidation reactions. Mixed metal oxides do not necessarily follow this general trend; *e.g.*, $CuO/Cr_2O_3$ has been found to be more active than $MnO_2/Cr_2O_3$ in some reactions (Laidig *et al.*, 1981).

There are very few studies that examine the reaction pathway for the oxidation of chlorinated hydrocarbons, particularly at temperatures below about 400°C. In general, reaction conditions are chosen that result in complete oxidation to $H_2O$, $CO_2$, and HCl. Also, most studies do not report comprehensive analysis of the products of oxidation, which would allow some speculation as to the reaction pathway.

Since little has been reported on the reaction pathways and product distribution in the catalytic oxidation of low concentrations of chlorinated compounds in air, the objective of this study is to investigate the catalytic oxidation of 1,1-dichloroethane in air at temperatures from 30 to 500°C over a commercial catalyst.

## EXPERIMENTAL

### *Equipment and Materials*

Figure 1 is a schematic representation of the experimental setup. An AMETEK Instruments residual gas analyzer (RGA) with a quadrupole mass detector capable of detecting species to mass 200 was the heart of the analytical system. The reactor was a 1/4" o.d. quartz tube which was loaded with 70 to 80 mg catalyst between glass wool plugs. A Carle 111 gas chromatograph with flame ionization and thermal conductivity detectors was used to crosscheck and calibrate the signals from the RGA. The chlorocarbons were obtained from Scott Specialty Gases, Plumsteadville, PA, as certified mixtures of 1000 ppm in air. Lower concentrations were obtained by diluting with hydrocarbon-free air (Union Carbide Linde Division; grade 0.1) through mass flow controllers which were calibrated against soap bubble flow meters before each run. The catalyst, consisting of 15–25% $Cr_2O_3$ supported on $Al_2O_3$ (Hunter *et al.*,

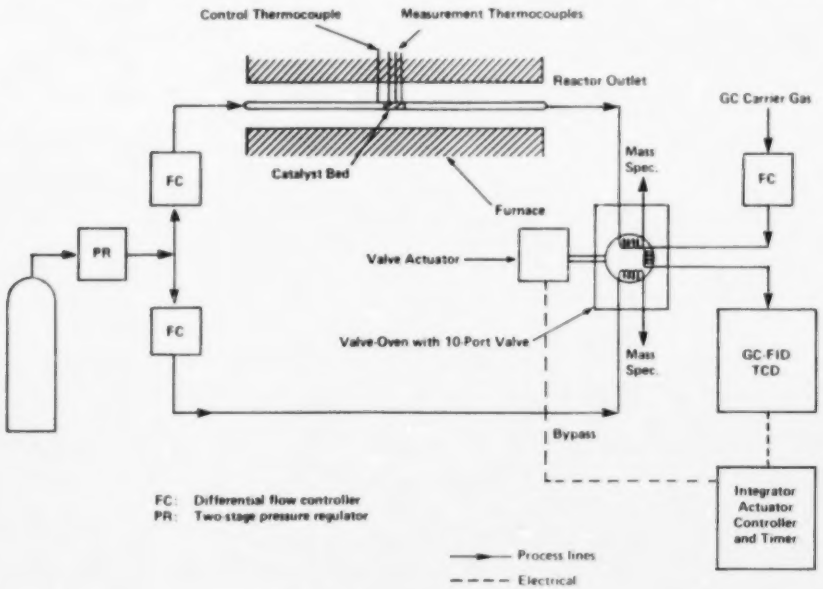


FIGURE 1 Microreactor system.

1982), was obtained from ARI Technologies, who market a fluidized bed catalytic incinerator system for the destruction of chlorinated hydrocarbons. The catalyst was ground and sieved to 150/200 mesh for all experiments.

*Procedure*

Two different sets of experiments were carried out in the course of this study. Initially, reaction products were continuously monitored on the mass spectrometer while heating the reactor at a linear rate (10°C $min^{-1}$) from 30 to 500°C. Experiments at lower heating rates established that this rate was low enough to allow local equilibrium to be attained at the catalyst surface. These experiments identified the conditions for maxima and minima in the concentration of different intermediates and products.

The second set of experiments consisted of steady state, isothermal activity measurements to measure the concentrations of different species formed at these conditions. Drager tubes were used in conjunction with gas chromatography to analyze reaction products and to carry out the material balance on the system. Drager tubes are accurate to about ±15%. Previously reported techniques by Manning (1984) and Weldon and Senkan (1986) for the analysis of HCl and $Cl_2$ mixtures in air proved unsatisfactory at the lower concentration levels of this study. Hence, efforts were focused on closing the material balance on carbon and accounting for all the carbon-chlorine bonds. The analysis of HCl and $Cl_2$ is part of our current effort and will be the subject of a later paper.

A 6′ × 1/8″ column packed with 3% SP1500 on 60/80 mesh Carbopak B was used with the flame ionization detector (FID) for analysis of hydrocarbons, and a 6′ × 1/8″ column packed with Porapak N (60/80 mesh) was used with the thermal conductivity detector (TCD) for carbon dioxide analysis. No carbon monoxide was detected in any of the experiments.

## RESULTS

All results reported are for streams of 500 ppm chlorocarbon in air at one atmosphere and a flow rate of 200 cc $min^{-1}$, which corresponds to a space velocity of $1.4 \times 10^5$ $hr^{-1}$. Experiments conducted at higher flow rates did not cause a change in peak temperatures or the global reaction rate, indicating the absence of external mass transfer effects. Damkohler numbers were calculated to be 0.045 at 500°C and 0.063 at 300°C suggesting negligible intraparticle mass transfer effects.

Figure 2 shows the effect of temperature on the relative levels of different compounds in the reactor effluent. The baselines are shifted on the figure; hence, the apparent presence of $CO_2$, $Cl_2$, and HCl at low temperatures is an artifact of the way the data are plotted. Homogeneous reactions would not be expected under the conditions of this study. This was verified with experiments in the absence of catalyst. Because the sensitivity of the RGA is different for each of the compounds shown in Figure 2, the intensities on the *y*-axis do not correspond to the relative concentration of any compound compared to another. For instance, the sensitivity of the RGA is lower for HCl than chlorine. At 500°C, the concentrations of HCl and chlorine are approximately equal, as determined by Drager tube analysis, but the intensities of the ions corresponding to chlorine are much higher than for HCl. Nevertheless, an increase (or decrease) in intensity for any one compound as a function of temperature does, of course, represent an increase (or decrease) in concentration of that

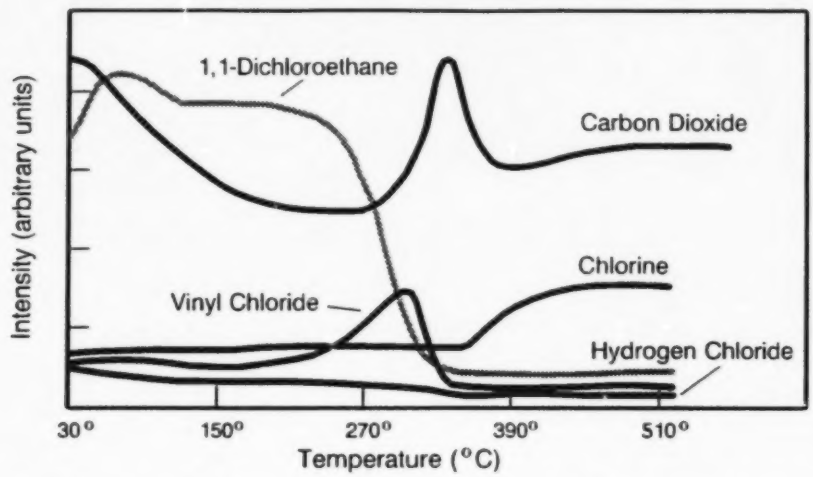


FIGURE 2 Product distribution in the catalytic oxidation of 1,1-dichloroethane; heating rate 10°C $min^{-1}$; inlet concentration 500 ppm.

compound. The signal intensities are in arbitrary units and have been plotted on the same figure to clearly show the relative positions of maxima of different species.

The spectra for the different compounds were obtained simultaneously while ramping the reactor temperature at 10°C $min^{-1}$. The concentration of 1,1-dichloroethane does not drop off appreciably from the inlet level of 500 ppm until about 230°C and destruction is essentially complete at about 330°C. Measurable levels of vinyl chloride are detected at about 230°C, when 1,1-dichloroethane first starts to react. The vinyl chloride concentration passes through a maximum at about 300°C and then drops abruptly below the detection limit at about 330°C.

To measure reactant and product concentration more accurately so that a material balance could be carried out, experiments were conducted under isothermal conditions at temperatures of 30 to 500°C. Reactor outlet concentrations of 1,1-dichloroethane, vinyl chloride and carbon dioxide were measured at steady state on a gas chromatograph. The trends in concentration levels suggested in Figure 2 were reproduced well. The maximum concentration of vinyl chloride measured on the gas chromatograph (at 300°C) is between 100 and 150 ppm, which agrees well with Drager tube measurements. The 1,1-dichloroethane concentration is about 100 ppm at this temperature.

Neither hydrogen chloride nor chlorine appears to be formed to any appreciable extent until vinyl chloride decomposition commences at about 330°C, but since the sensitivity of the RGA for both chlorine and hydrogen chloride is low, these compounds may be present at lower temperatures. Drager tube measurements indicate HCl and $Cl_2$ concentrations of 250 to 300 ppm each at 500°C. At 300°C, no chlorine can be detected by Drager tubes and the HCl concentration is 400 to 500 ppm.

$CO_2$ formation peaks after the vinyl chloride peak disappears ($\sim$350°C). Steady state experiments were carried out to determine $CO_2$ concentrations at 300 and 500°C: 350 to 400 ppm carbon dioxide are formed at 300°C and 1000 ppm are produced at 500°C.

## DISCUSSION

Table I represents the material balance on carbon atoms at 300°C and 500°C. These temperatures were selected as representing (1) peak vinyl chloride concentration (300°C); and (2) the highest temperature in the study (500°C). For complete oxidation, each mole of 1,1-dichloroethane would yield two moles of carbon dioxide. Neglecting the change in total volume of the gas due to the large excess of air, the $CO_2$ concentration should be twice the inlet concentration of 1,1-dichloroethane if all carbon were converted to $CO_2$. Table I shows that this is indeed the case at 500°C, with 1000 ppm of $CO_2$ being formed from 500 ppm of 1,1-dichloroethane.

At 300°C, the material balance on carbon atoms can be closed to within 10% with vinyl chloride, carbon dioxide and unreacted 1,1-dichloroethane. It appears that all carbon–chlorine bonds at this temperature occur in either vinyl chloride or 1,1-dichloroethane.

The inaccuracies inherent in Drager tube measurements limit the closure of the material balance on chlorine. Table II represents the material balance on chlorine atoms at 300°C and 500°C. Drager tube measurements at 300°C indicate no measurable chlorine and 400 to 500 ppm hydrogen chloride. Assuming the higher value, the chlorine balance can be closed to within 15% with vinyl chloride, 1,1-dichloroethane and hydrogen chloride. Current efforts are focused on improving the analytical procedure for chlorine and hydrogen chloride measurements in order to close the material balance on the whole system.

At 500°C, both chlorine and hydrogen chloride are present at levels of 200 to 250 ppm. Assuming the higher value in both cases closes the chlorine balance to only 25%. Since the carbon balance at this temperature indicates no carbon-chlorine bonds, the most likely explanation for the discrepancy is the formation of species such as chlorine monoxide or chlorine dioxide, which were detected on the RGA but were not measured quantitatively. It is also possible that the catalyst is reacting with HCl and $Cl_2$.

The presence of vinyl chloride suggests that abstraction of HCl (dehydrochlorination) is the first step in the reaction process. Vinyl chloride, being very stable, does not undergo further dehydrochlorination, and oxidizes to $CO_2$, HCl, $Cl_2$ and $H_2O$. Further, evidence of the HCl abstraction mechanism has been found in preliminary experiments on the oxidation of 1,1,1-trichloroethane, where 1,1-dichloroethylene has been identified as an intermediate on this catalyst as shown in Figure 3. The baselines are shifted on this figure as well, so $CO_2$, $Cl_2$ and HCl formation at low temperatures does not occur. The apparent presence of 1,1-dichloroethylene at low temperatures is due to a common ion (M/e = 61) in the mass spectra of 1,1,1-trichloroethane and 1,1-dichloroethylene. Experiments using gas chromatography showed no 1,1-dichloroethylene until about 180°C. Michalowicz (1982) observed polymerization in the

TABLE I
Material balance on carbon atoms

| Species | 1,1-Dichloroethane Conc. (ppm) | 1,1-Dichloroethane g atoms C ($\times 10^6$) | Vinyl Chloride Conc. (ppm) | Vinyl Chloride g atoms C ($\times 10^6$) | Carbon Dioxide Conc. (ppm) | Carbon Dioxide g atoms C ($\times 10^6$) | Total g atoms C ($\times 10^6$) |
|---|---|---|---|---|---|---|---|
| 300°C In | 500 | 1000 | 0 | 0 | 0 | 0 | 1000 |
| Out | 100 | 200 | 150 | 300 | 400 | 400 | 900 |
| 500°C In | 500 | 1000 | 0 | 0 | 0 | 0 | 1000 |
| Out | 0 | 0 | 0 | 0 | 1000 | 1000 | 1000 |

TABLE II
Material balance on chlorine atoms

| Species | 1,1-Dichloroethane | | Vinyl Chloride | | Hydrogen Chloride | | Chlorine | | Total |
|---|---|---|---|---|---|---|---|---|---|
| | Conc. (ppm) | g atoms Cl ($\times 10^6$) | Conc. (ppm) | g atoms Cl ($\times 10^6$) | Conc. (ppm) | g atoms Cl ($\times 10^6$) | Conc. (ppm) | g atoms Cl ($\times 10^6$) | g atoms Cl $\times 10^6$ |
| 300°C In | 500 | 1000 | 0 | 0 | 0 | 0 | 0 | 0 | 1000 |
| Out | 100 | 200 | 150 | 150 | 500 | 500 | 0 | 0 | 850 |
| 500°C In | 500 | 1000 | 0 | 0 | 0 | 0 | 0 | 0 | 1000 |
| Out | 0 | 0 | 0 | 0 | 250 | 250 | 250 | 500 | 750 |

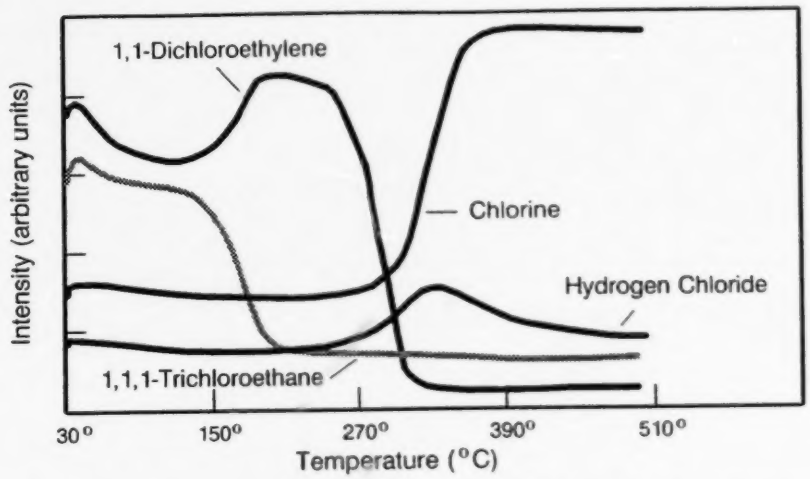


FIGURE 3 Product distribution in the catalytic oxidation of 1,1,1-trichloroethane; heating rate 10°C $min^{-1}$; inlet concentration 500 ppm.

catalytic oxidation of trichloroethylene over a $Cr_2O_3/Al_2O_3$ catalyst. This suggests the formation of triply bonded carbon species (coke) by a mechanism such as dehydrochlorination.

Earlier research has provided insight into how a few chlorinated hydrocarbons are oxidized, though no general mechanism has been established. Palazzolo *et al.* (1986) showed the presence of 1,2-dichloroethylene in the oxidation of a mixture of chlorinated hydrocarbons containing 1,1,2-trichloroethane, among other chlorinated hydrocarbons, over a "commercial metal oxide catalyst supported on alumina," suggesting that HCl abstraction may be one step in the oxidation of 1,1,2-trichloroethane. However, since other two-carbon chlorinated species were present, it is impossible to attribute the presence of 1,2-dichloroethylene to HCl abstraction from 1,1,2-trichloroethane. Christian and Johnson (1965) also observed HCl abstraction producing 1,1-dichloroethylene in the oxidation of 1,1,1-trichloroethane over a hopcalite (78.3% $MnO_2$–13.1% CuO) catalyst, although 1,1,2-trichloroethylene was also formed. Similarly, Lavanish and Sare (1977) observed an increase in 1,1-dichloroethylene concentration over a hydrated nickel oxide catalyst in the oxidation of a mixture containing 1,1-dichloroethylene and 1,1,1-trichloroethane, among other chlorinated hydrocarbons. They attribute this increase in 1,1-dichloroethylene concentration to HCl abstraction from 1,1,1-trichloroethane. The fact that these observations were made at low temperatures ($< 104$°C) and that the amount of 1,1-dichloroethylene in excess of that entering the reactor decreased with increasing temperature suggests that HCl abstraction may be a first step in 1,1,1-trichloroethane oxidation on this catalyst. A similar conclusion is suggested by analogous studies on a cobalt/manganese catalyst (Sare and Lavanish, 1977a).

A two-step process may be postulated based on the experimental observations:

$$C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl \quad (1)$$

$$C_2H_3Cl + 5/2\ O_2 \rightarrow 2\ CO_2 + HCl + H_2O \quad (2)$$

which sum up to:

$$C_2H_4Cl_2 + 5/2\ O_2 \rightarrow 2\ CO_2 + 2\ HCl + H_2O \quad (3)$$

The presence of chlorine can be explained by the Deacon reaction (Weldon and Senkan, 1986):

$$2\ HCl + 1/2\ O_2 \rightarrow H_2O + Cl_2 \quad (4)$$

Previous work on the catalytic oxidation of chlorinated hydrocarbons has concentrated on single carbon species such as methylene chloride and chloroform. Both Manning (1984) and Weldon and Senkan (1986) report significant amounts of carbon monoxide formation from these compounds over $Cr_2O_3/Al_2O_3$ catalysts. This was not observed in our study. The double bonded species formed in the initial stages of the reaction are more reactive than the single carbon compounds, leading to complete oxidation to carbon dioxide.

An alternative explanation for the absence of carbon monoxide in our study is suggested by the work of Michalowicz (1982). The selectivity for carbon dioxide versus carbon monoxide formation in the oxidation of chlorinated ethylenes over a $Cr_2O_3/Al_2O_3$ catalyst was found to decrease with increasing chlorocarbon concentration. Competition of carbon monoxide with the chlorocarbon for oxidation sites was suggested as an explanation of this phenomenon. The range of reactant concentrations in the studies of Manning (1984), Weldon and Senkan (1986), and Michalowicz (1982) spanned 3000 to 40 000 ppm. Based on the observations of Michalowicz (1982), the concentration of 500 ppm 1,1-dichloroethane used in our study would favor carbon dioxide formation over carbon monoxide.

## CONCLUSIONS

- No carbon-chlorine bonds are present when 1,1-dichloroethane is oxidized over the commercial catalyst studied at 500°C. HCl and $Cl_2$ are the only chlorine-containing products formed at this temperature. They appear to be produced in equal quantities, although more work needs to be done to better determine the exact concentrations.
- Significant amounts (> 100 ppm) of vinyl chloride are formed at temperatures between 230 and 330°C. This, together with the sequential appearance of vinyl chloride, hydrogen chloride and chlorine product peaks, suggests that dehydrochlorination is the first step in the oxidation of 1,1-dichloroethane. The identification of 1,1-dichloroethylene as an intermediate in the oxidation of 1,1,1-trichloroethane supports this hypothesis.

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